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(54) Title: ESTERIFICATION CATALYST COMPOSITIONS

(57) Abstract: A catalyst composition suitable for use as a catalyst for the preparation of an ester, including a polyester, comprises an organometallic compound which is a complex of first metal selected from the group consisting of titanium and zirconium, a second metal selected from the group consisting of germanium, antimony and tin and a carboxylic acid, preferably in the presence of an alcohol having at least two hydroxy groups and a base. The catalyst composition may further comprise a dihydric alcohol and a base.

### ESTERIFICATION CATALYST COMPOSITIONS

The invention concerns esterification catalyst compositions and in particular esterification catalyst compositions which comprise novel organometallic compositions based on a combination of titanium or zirconium with other metals.

Organotitanium compounds and, in particular, titanium alkoxides or orthoesters are known as catalysts for esterification processes. During the esterification, these compounds are frequently converted to insoluble compounds of titanium which result in a hazy product. The presence of a haze is a particular disadvantage in polyesters which have a high viscosity and/or high melting point and are therefore difficult to filter. Furthermore, many organotitanium compounds which are effective catalysts in the manufacture of polyesters such as polyethylene terephthalate are known to produce unacceptable yellowing in the final polymer. GB-A-2314081 relates to an esterification process in which these problems are partially solved but there is still a need for a catalyst which induces little or no yellowing in a polyester produced using the catalyst.

It is an object of the present invention to provide an improved catalyst for a process for preparing esters.

According to the invention, a catalyst composition suitable for use as a catalyst for the preparation of an ester comprises an organometallic compound which is a complex of a first metal selected from the group consisting of titanium or zirconium, a second metal selected from the group consisting of germanium, antimony or tin, and a carboxylic acid.

Also according to the invention, a process for the preparation of an ester comprises carrying out an esterification reaction in the presence of a catalyst composition comprising an organometallic compound which is a complex of a first metal selected from the group consisting of titanium and zirconium, a second metal selected from the group consisting of germanium, antimony and tin, and a carboxylic acid.

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The first metal is titanium or zirconium and, preferably, is titanium.

The second metal is selected from the group consisting of germanium, antimony and tin but is preferably germanium or antimony. It is preferably present in an amount such that the molar ratio of first metal to second metal is in the range 99 : 1 to 1 : 99. More preferably, the molar ratio of first metal to second metal is in the range 50 : 1 to 1 : 50.

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A number of carboxylic acids, having one or more than one carboxyl group, can be used to form the complexes which comprise the catalysts of the invention, but preferably, the acid contains from 1 to 20, more preferably from 1 to 12 carbon atoms. Suitable unsubstituted carboxylic acids include acetic acid, oxalic acid, capric acid and lauric acid. A useful class of acids is hydroxy carboxylic acids and, preferably, 2-hydroxy carboxylic acids. In this class, preferred acids include lactic acid, citric acid, malic acid and tartaric acid. The preferred molar ratio of acid to total metal in the complex is 4 : 1 to 0.1 : 1 more preferably from 3 : 1 to 0.25 : 1.

Preferably, the catalyst composition of the invention includes as a further component a solubilising compound. A preferred solubilising compound is an alcohol containing at least two hydroxyl groups. Preferably the alcohol is a dihydric alcohol and may be a 1,2-diol such as 1,2-ethanediol or 1,2-propanediol, a 1,3-diol such as 1,3-propanediol, a 1,4-diol such as 1,4-butanediol, a diol containing non-terminal hydroxyl groups such as 2-methyl-2,4-pentanediol, cyclohexane dimethanol, or a dihydric alcohol containing a longer chain such as diethylene glycol or a polyethylene glycol. Preferred dihydric alcohols are 1,2-ethanediol and diethylene glycol. The organometallic compound can also be prepared from a polyhydric alcohol such as glycerol, trimethylolpropane or pentaerythritol. The catalyst composition is useful in the preparation of polyesters from dicarboxylic acids or esters thereof and di- or polyhydric alcohols, and when the catalyst is intended to be used in such reactions, it may be beneficial to use as the alcohol component of the catalyst composition the alcohol which is to be used to make the polyester. When present, the solubilising compound is present in the complex in a ratio of from 50 to 1 moles of alcohol to each mole of total metal, i.e. the sum of the moles of the first and second metals. More preferably, the complex contains from 40 to 5 moles of alcohol per mole of total metal.

A base may also be used in preparing the complex which is the catalyst composition of the invention. The base may be useful to stabilise the complex and/or neutralise the acidic component. Suitable inorganic bases include sodium hydroxide, potassium hydroxide, calcium hydroxide and ammonium hydroxide. Preferred organic bases include quaternary ammonium compounds such as tetrabutyl ammonium hydroxide, tetraethyl ammonium hydroxide (TEAH), choline hydroxide (trimethyl(2-hydroxyethyl)ammonium hydroxide) or benzyltrimethyl ammonium hydroxide, or alkanolamines such as monoethanolamine, diethanolamine, triethanolamine and triisopropanolamine. Particularly preferred organic bases include choline hydroxide and TEAH, which have been found to produce polyester having particularly good colour properties when used in the catalysts of the invention. When present, the amount of base used is usually in the range 10 to 0.1 mole of base per mole of total metal. The preferred amount is in the range 3 to 0.25 mole base per mole of total metal.

The complexes of the invention can be prepared by a variety of methods. A suitable source of the first metal is an orthoester or condensed orthoester of titanium or zirconium. Preferably, the orthoester has the formula  $M(OR)_4$  where M is titanium or zirconium and R is an alkyl group. More preferably, R contains 1 to 6 carbon atoms and particularly suitable orthoesters include tetraisopropoxy titanium, 5 tetra-n-butoxy titanium, tetra-n-propoxy zirconium and tetra-n-butoxy zirconium.

Condensed orthoesters suitable for preparing the organometallic compounds used in this invention are typically prepared by careful hydrolysis of titanium or zirconium orthoesters. Titanium or zirconium condensed orthoesters are frequently represented by the formula  $R'O[M(OR')_2O]_nR'$  in which R' 10 represents an alkyl group and M represents titanium or zirconium. Preferably, n is less than 20 and more preferably is less than 10. Preferably, R' contains 1 to 12 carbon atoms, more preferably, R' contains 1 to 6 carbon atoms and useful condensed orthoesters include the compounds known as polybutyl titanate, polyisopropyl titanate and polybutyl zirconate.

15 One method of preparing a complex consists of reacting an orthoester or condensed orthoester of the first metal with the hydroxy acid and a suitable source of the second metal. Typically the source of the second metal is a compound including an alkoxide, oxide, halide or a metal-organic compound e.g. an organic salt or complex of the second metal, such as  $GeO_2$ ,  $Sb_2O_3$  or  $Bu_2SnO$  (butyl tin oxide),  $GeCl_4$ ,  $SbCl_3$  or  $SnCl_4$ ,  $Sb(OAc)_3$  (where Ac = acetyl), dibutyltin dilaurate or butyl tin acetate. These raw 20 materials may be mixed and refluxed before by-product alcohol (e.g. isopropanol when the orthoester is tetraisopropoxy titanium) is removed, usually by distillation. The base and alcohol containing at least two hydroxyl groups may then be added and, if necessary, further by-product alcohol removed. In a preferred embodiment, the catalysts may be derived from an alkoxide of the second metal (e.g.  $Ge(OR')_4$ , where R' has the same meaning as given above, e.g. germanium isopropoxide. Other 25 reaction sequences starting from these raw materials can be used and these will be apparent to a skilled person.

In an alternative preparation a derivative of the second metal with the carboxylic acid (for example, germanium citrate) is prepared, usually with the addition of a solvent e.g. water or another solvent e.g. 30 an alcohol such as ethanol or methanol, to dissolve the acid, and this is then reacted with the product derived from mixing together the alcohol containing at least two hydroxyl groups, the base and an orthoester or condensed orthoester of the first metal. By-product alcohol and water may be removed during the preparation, normally by distillation. Other reaction sequences are envisaged as will be understood by those skilled in organometallic chemistry.

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The esterification reaction of the process of the invention can be any reaction by which an ester is produced. The reaction may be (i) a direct esterification in which a carboxylic acid or its anhydride

and an alcohol react to form an ester or (ii) a transesterification (alcoholysis) in which a first alcohol reacts with a first ester to produce an ester of the first alcohol and a second alcohol produced by cleavage of the first ester or (iii) a transesterification reaction in which two esters are reacted to form two different esters by exchange of alkoxy radicals. Direct esterification or transesterification can be used in the production of polymeric esters and a preferred process of the invention comprises a polyesterification process. Many carboxylic acids and anhydrides can be used in direct esterification including saturated and unsaturated monocarboxylic acids and anhydrides of such acids such as stearic acid, isostearic acid, capric acid, caproic acid, palmitic acid, oleic acid, palmitoleic acid, triacontanoic acid, benzoic acid, methyl benzoic acid, salicylic acid and rosin acids such as abietic acid, dicarboxylic acids such as phthalic acid, isophthalic acid, terephthalic acid, sebacic acid, adipic acid, azelaic acid, succinic acid, fumaric acid, maleic acid, naphthalene dicarboxylic acid and anhydrides of these acids and polycarboxylic acids such as trimellitic acid, citric acid, trimesic acid, pyromellitic acid and anhydrides of these acids. Alcohols frequently used for direct esterification include aliphatic straight chain and branched monohydric alcohols such as butyl, pentyl, hexyl, octyl and stearyl alcohols, dihydric alcohols such as 1,2-ethanediol, 1,3-propanediol, 1,4-butanediol and 1,6-hexanediol, 1,4-cyclohexane dimethanol and polyhydric alcohols such as glycerol and pentaerythritol.

The esters employed in an alcoholysis reaction are generally the lower homologues such as methyl, ethyl and propyl esters since, during the esterification reaction, it is usual to eliminate the displaced alcohol by distillation. These lower homologue esters of the acids suitable for direct esterification are suitable for use in the transesterification process according to the invention. Frequently (meth)acrylate esters of longer chain alcohols are produced by alcoholysis of esters such as methyl acrylate, methyl methacrylate, ethyl acrylate and ethyl methacrylate. Typical alcohols used in alcoholysis reactions include butyl, hexyl, n-octyl and 2-ethyl hexyl alcohols and substituted alcohols such as dimethylaminoethanol.

When the esterification reaction is a transesterification between two esters, generally the esters will be selected so as to produce a volatile product ester which can be removed by distillation.

As mentioned hereinbefore, polymeric esters can be produced by processes involving direct esterification or transesterification and a particularly preferred embodiment of the esterification process of the invention is a polyesterification reaction in the presence of the catalyst composition described hereinbefore. In a polyesterification reaction polybasic acids or esters of polybasic acids are usually reacted with polyhydric alcohols to produce a polymeric ester. Linear polyesters are often produced from dibasic acids such as those mentioned hereinbefore or esters of said dibasic acids and dihydric alcohols. Preferred polyesterification reactions according to the invention include the reaction

- of terephthalic acid or dimethyl terephthalate, optionally with a proportion of the isophthalate or isophthalic acid, with 1,2-ethanediol (ethylene glycol) to produce polyethylene terephthalate or with 1,3-propanediol (propylene glycol) to produce polypropylene terephthalate, also known as polytrimethylene terephthalate or with 1,4-butanediol (butylene glycol) to produce polybutylene
- 5 terephthalate or reaction of naphthalene dicarboxylic acid or dimethyl naphthalate with 1,2-ethanediol to produce polyethylene naphthalate. Other acids, such as isophthalic acid and other glycols such as 1,4-cyclohexane dimethanol and polyhydric alcohols such as glycerol, trimethylolpropane and pentaerythritol are also suitable for preparing polyesters. Mixed polyesters, i.e. copolymers, may be made by selecting more than one type of dibasic acid, anhydride or ester starting material and/or
- 10 more than one type of alcohol as is well known in the art.

The esterification reaction of the invention can be carried out using any appropriate, known technique for an esterification reaction.

- 15 A typical process for the preparation of polyethylene terephthalate comprises two stages. In the first stage terephthalic acid or dimethyl terephthalate is reacted with 1,2-ethanediol to form a prepolymer and the by-product water or methanol is removed. The prepolymer is subsequently heated in a second stage to remove 1,2-ethanediol and form a long chain polymer. Either or both these stages may comprise an esterification process according to this invention. Processes may be operated
- 20 either on a batch or a continuous basis.

In direct esterification the acid or anhydride and an excess of alcohol are typically heated, if necessary in a solvent, in the presence of the catalyst composition. Water is a by-product of the reaction and this is removed, as an azeotrope with a boiling mixture of solvent and/or alcohol.

- 25 Generally, the solvent and/or alcohol mixture which is condensed is at least partially immiscible with water which is therefore separated before solvent and/or alcohol are returned to the reaction vessel. When the reaction is complete the excess alcohol and, when used, solvent are evaporated. In view of the fact that the catalyst compositions of the invention do not normally form insoluble species, it is not generally necessary to remove them from the reaction mixture, as is frequently necessary with
- 30 conventional catalysts. A typical direct esterification reaction is the preparation of bis(2-ethylhexyl) phthalate which is prepared by mixing phthalic anhydride and 2-ethyl hexanol. An initial reaction to form a monoester is fast, but the subsequent conversion of the monoester to diester is carried out by refluxing in the presence of the catalyst composition at a temperature of 180 -210° C until all the water has been removed. Subsequently the excess alcohol is removed.

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In an alcoholysis reaction, the ester, first alcohol and catalyst composition are mixed and, generally, the product alcohol (second alcohol) is removed by distillation, often as an azeotrope with the ester.

Frequently it is necessary to fractionate the vapour mixture produced from the alcoholysis in order to ensure that the second alcohol is separated effectively without significant loss of product ester or first alcohol. The conditions under which alcoholysis reactions are carried out depend principally upon the components of the reaction and generally components are heated to the boiling point of the mixture used.

A preferred process of the invention is the preparation of polyethylene terephthalate. A typical batch production of polyethylene terephthalate is carried out by charging terephthalic acid and ethylene glycol to a reactor along with catalyst composition, if desired, and heating the contents to 260 - 270° C under a pressure of about 0.3 Mpa (40 psi). Reaction commences as the acid dissolves and water is removed. The product is transferred to a second autoclave reactor and catalyst composition is added, if needed. The reactor is heated to 285 - 310° C under an eventual vacuum of 100 Pa (1 mbar) to remove ethylene glycol by-product. The molten product ester is discharged from the reactor, cooled and chipped. The chipped polyester may be then subjected to solid state polymerisation, if appropriate.

A preferred means of adding the catalyst compositions of this invention to a polyesterification reaction is in the form of a solution in the glycol being used (e.g. ethylene glycol in the preparation of polyethylene terephthalate). This method of addition is applicable to addition of the catalyst composition to the polyesterification reaction at the first stage or at the second stage.

The amount of catalyst used in the esterification process of the invention generally depends upon the total metal content (expressed as amount of first metal plus amount of second metal) of the catalyst composition. Usually the amount is from 50 to 400 parts per million (ppm) of total metal based on weight of product ester for direct or transesterification reactions. Preferably, the amount is from 75 to 300 ppm of total metal based on weight of product ester. In polyesterification reactions the amount used is generally expressed as a proportion of the weight of product polyester and is usually from 3 to 500 ppm expressed as total metal (first metal plus second metal) based on product polyester. Preferably, the amount is from 5 to 300 ppm expressed as total metal based on product polyester.

As is known, it is common to add a colour managing compound to the polyesterification reaction in order to counteract any yellowing which may occur in the finished polymer product. Commonly the compound used is a cobalt compound and this may be done in the preparation of PET by e.g. adding cobalt acetate tetrahydrate in glycol in an amount up to 100 ppm, preferably 0 - 75 ppm. Alternative or additional colour managing compounds include organic dyes.

Normally phosphorus stabilisers are added to polyester at the polyesterification stage at a level of up to about 200 ppm, preferably 0 – 100 ppm. The amount used is carefully controlled in order to avoid poisoning the esterification catalysts. The phosphorous may be added in many forms, including phosphoric acid, phosphorous acid, phosphate esters, phosphonic acids, pyrophosphates, phosphites and others known in the art.

Additional compounds may be added to the polyesterification reaction if required. Such additives include dyes, optical brighteners, pigments, dye pretreatments, reheat agents and delustrants such as titanium dioxide. Solid state polymerisation accelerators may also be added. It may also be required to control the co-products of the polyesterification process, in particular the diethylene glycol (DEG) content of the polymer, by addition of DEG suppressants such as bases or amines, as is known in the art. The DEG content of the polymer is believed to affect the thermal properties of the polymer. For certain applications, the DEG content should be low although for textile fibre it may be desirable to control the level of DEG to 0.8 – 1.5 weight %

The products of this invention have been shown to be effective catalyst compositions for producing esters and polyesters at an economical rate without leading to haze in the final product and with a reduced amount of yellowing of polyesters in comparison to known catalysts. The invention is illustrated by the following examples.

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#### Preparation of organometallic complexes for use as catalysts

##### Example 1

Citric acid monohydrate (131.34 g, 0.625 moles) were placed in a reaction flask with 100 g of demineralised water and stirred for approximately 15 minutes. To the solution was added titanium isopropoxide (63.95 g, 0.225 moles) and germanium iso-propoxide (7.72 g, 0.025 moles), over 30 minutes. The mixture was then heated to reflux for 60 minutes and left to stir overnight with no heating. The product was then distilled at atmospheric pressure to remove water/isopropanol. The resultant solution was allowed to cool to room temperature and then 32% wt aqueous sodium hydroxide solution (95g, 0.76 moles) was added to it over 30 minutes. The solution was then diluted with ethylene glycol (125.35 g, 2.02 moles) and stirred for 20 minutes. The product was filtered and a second distillation was then carried out under reduced pressure to remove remaining isopropanol and water. The product was a colourless, highly viscous solution having a Ti content of 3.76% wt and a Ge content of 0.63% wt. To ease handling the product was later diluted with an equal weight of monoethylene glycol.

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##### Example 2



37.81 g of citric acid monohydrate (0.180 moles) were placed in a reaction flask with 28.79 g of demineralised water and stirred for 15 minutes. To the solution was added 2.05 g of titanium isopropoxide (0.0072 moles) and 20.00 g of germanium isopropoxide (0.064 moles) over 30 minutes. The mixture was then heated to reflux for 60 minutes and left to stir overnight with no heating. The product was then distilled at atmospheric pressure to remove water/isopropanol. The resultant solution was allowed to cool to room temperature and then 32% wt aqueous sodium hydroxide solution (27.35 g, 0.219 moles) added to it over 30 minutes. The solution was then diluted with ethylene glycol (36.09 g, 0.582 moles) and stirred for 20 minutes. The product was filtered and a second distillation was then carried out under reduced pressure to remove remaining isopropanol and water. The product was a green mobile solution having a Ti content of 0.44% wt and a Ge content of 5.93% wt

### Example 3

A germanium citrate was prepared as follows: germanium dioxide (3.952 g, 0.0378 moles) was placed in a round-bottomed flask and suspended in water (14 g). After stirring for 15 minutes, citric acid monohydrate (22.0 g, 0.105 moles) was added over 20 minutes. The resulting mixture was stirred for 90 minutes at room temperature, then heated to 85° C over 240 minutes and then allowed to cool to room temperature overnight. The product was diluted with monoethylene glycol (15.6 g) to yield a clear solution having a Ge content of 4.94% by weight.

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Monoethylene glycol (44.7 g, 0.72 mole) was added to titanium tetra-n-butoxide (6.18 g, 0.018 mole) in a beaker and stirred for 20 minutes. 32% wt aqueous sodium hydroxide solution (2.16 g, 0.018 mole) was added dropwise over 10 minutes followed by the germanium citrate solution (2.94 g, 0.002 mole Ge) over a further 10 minutes to yield a clear colourless solution. This product contained 1.55% Ti and 0.26% Ge by weight.

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### Example 4

Monoethylene glycol (37.25 g, 0.60 mole) was added to titanium tetra-n-butoxide (5.10 g, 0.015 mole) in a beaker and stirred for 20 minutes. 32% wt aqueous sodium hydroxide solution (1.80 g, 0.015 mole) was added dropwise over 10 minutes followed by germanium citrate solution as prepared in Example 3 (7.35 g, 0.005 mole Ge) over a further 10 minutes to yield a clear colourless solution. This product contained 1.40% Ti and 0.70% Ge by weight.

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### Example 5

Monoethylene glycol (24.85 g, 0.40 mole) was added to titanium tetra-n-butoxide (3.40 g, 0.01 mole) in a beaker and stirred for 20 minutes. 32% wt aqueous sodium hydroxide solution (1.2 g, 0.01 mole) was added dropwise over 10 minutes followed by germanium citrate solution prepared as in Example

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3 above (14.7 g, 0.01 mole Ge) over a further 10 minutes to yield a clear colourless solution. This product contained 1.09% Ti and 1.64% Ge by weight.

#### **Example 6**

- 5 Monoethylene glycol (12.42 g, 0.2 mole) was added to titanium tetra-n-butoxide (1.7 g, 0.005 mole) in a beaker and stirred for 20 minutes. 32% wt aqueous sodium hydroxide solution (0.60 g, 0.005 mole) was added dropwise over 10 minutes followed by germanium citrate solution prepared as in Example 3 above (22.05 g, 0.015 mole Ge) over a further 10 minutes to yield a clear colourless solution. This product contained 0.65% Ti and 2.96% Ge by weight.

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#### **Example 7**

- A germanium oxalate was prepared as follows. Germanium dioxide (3.986 g) was placed in a round-bottomed flask and suspended in water (14.0 g). After stirring for 15 minutes, oxalic acid (10.33 g, 0.115 moles) was added slowly over 20 minutes. The resulting mixture was stirred for 15 minutes at room temperature then heated to 85° C over 240 minutes. Finally it was allowed to cool to room temperature overnight. The product was diluted with monoethylene glycol (15.6 g) to yield a clear solution having a Ge content of 6.31% by weight.

- 20 Monoethylene glycol (37.25 g, 0.60 mole) was added to titanium tetra-n-butoxide (5.10 g, 0.015 mole) in a beaker and stirred for 20 minutes. 32% wt aqueous sodium hydroxide solution (1.80 g, 0.01 mole) was added dropwise over 10 minutes followed by germanium oxalate solution prepared as above (5.75 g, 0.005 mole Ge) over a further 10 minutes to yield a clear colourless solution. This product contained 1.44% Ti and 0.73% Ge by weight.

#### **Example 8**

- 25 Monoethylene glycol (12.42 g, 0.20 mole) was added to titanium tetra-n-butoxide (1.70 g, 0.005 mole) in a beaker and stirred for 20 minutes. 32% wt aqueous sodium hydroxide solution (0.60 g, 0.005 mole) was added dropwise over 10 minutes followed by germanium oxalate solution prepared as in Example 7 above (17.24 g, 0.015 mole Ge) over a further 10 minutes to yield a clear colourless solution. This product contained 0.75% Ti and 3.40% Ge by weight.

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#### **Example 9 (Comparative)**

- 35 Citric acid monohydrate (132.5 g, 0.63 moles) was dissolved in water (92.8 g). To the stirred solution was slowly added titanium isopropoxide (72.0 g, 0.25 moles). This mixture was heated to reflux for 1 hour to yield a hazy solution. This solution stripped under vacuum to remove free water and isopropanol. The product was cooled below 70°C and 32 %w/w aqueous sodium hydroxide (94.9 g, 0.76 moles) was added slowly to the stirred solution. The product was filtered, mixed with ethylene

glycol (125.5 g, 2.0 moles) and heated under vacuum to remove free water/isopropanol. The product was a slightly hazy, very pale yellow liquid (Ti content 3.85 % by weight).

#### **Example 10**

- 5 4.20 g of antimony tris-glycollate (Elf Atochem S24 grade) and 131.0 g of the titanium compound made in Example 9 were combined to give a colourless suspension. Moderate heating for 2 hours yielded a clear pale yellow solution of the new titanium – antimony species (3.52 % w/w Ti, 1.77 % w/w Sb).

#### **Example 11**

##### **Preparation of polyethylene terephthalate**

- A polycondensation reaction was carried out in a mechanically-stirred 300 ml glass vessel fitted with side arm and cold trap for collection of monoethylene glycol. A thermostatically controlled ceramic heating element was used to provide heat and an oil vacuum pump was connected to the cold trap. A  
15 nitrogen blanket was provided via a connection to the cold trap.

- Polyethylene terephthalate was prepared from terephthalic acid-based prepolymer having a glycol : acid ratio of 1.3:1 and a degree of polymerisation of 6.5. 100 g of prepolymer was placed in the reaction flask under a nitrogen flow, followed by a dilute solution of catalyst component calculated on  
20 prepolymer weight to give the required level of metals, in monoethylene glycol. This was heated to 250° C and stirred for 25 minutes, at which point a monoethylene glycol solution of stabiliser was added (phosphoric acid, calculated to produce the equivalent of 32 or 16 ppm P in the mixture). The nitrogen flow was stopped and vacuum applied steadily to 200 mbar. After 25 minutes the temperature was increased steadily from 250° C to 290° C. As the reaction progressed the current required to  
25 maintain a constant stirrer speed increased up to a value of 109.5 mA, at which point reaction was deemed to be complete. If this current was not registered after 130 minutes, the reaction was stopped at that time. The vacuum was then broken with nitrogen and the molten polymer discharged and quenched into cold water. It was then dried for 12 hours at 65° C.

- 30 The colour of the polymer was measured using a Byk-Gardner Colourview spectrophotometer. A common model to use for colour expression is the Cielab L\*, a\* and b\* scale where the b\*-value describes yellowness. The yellowness of the polymer increases with b\*-value.

- The polymer intrinsic viscosities (I.V.s) were measured by glass capillary viscometry using 60/40  
35 phenol/1,1,2,2-tetrachlorethane as solvent.

The polymers were examined by  $^1\text{H}$  NMR spectroscopy to determine the amount of diethylene glycol (DEG) residues present in the polymer chain (expressed as weight per cent of polymer), the proportion of hydroxyl (OH) end groups present (expressed as number of end groups per 100 polymer repeating units) and the proportion of vinyl end groups (VEG) present (expressed as number of end groups per 100 polymer repeating units).

The number average molecular weight and molecular weight distribution were determined by gel permeation chromatography (GPC) of the polymer dissolved in orthochlorophenol.

- 10 The temperatures of glass transition, crystallisation and melting were determined by differential scanning calorimetry (DSC).

#### DSC analysis

Heat-cool differential scanning calorimetry (DSC) experiments on 're-quenched' samples were conducted as follows: 10mg samples were dried at  $80^\circ\text{C}$  in a vacuum oven. These dried samples were then held at  $290^\circ\text{C}$  for 2 minutes in a Perkin-Elmer DSC instrument, before being quenched onto the cold block ( $-40^\circ\text{C}$ ). The re-quenched samples were then subjected to a heat/hold 2minutes/cool procedure, at heating & cooling rates of  $20^\circ\text{C}/\text{minute}$  on a Perkin-Elmer DSC 7a. The cooling data quoted below have been corrected by adding  $2.8^\circ\text{C}$  to the computer-generated temperatures.

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Results based on additions of 30 ppm Ti and using the catalysts prepared according to Examples 1 and 2 are given in Table 1 below in which results on polymer made using and antimony triacetate [ $\text{Sb}(\text{OAc})_3$ ] (at an antimony level of 250 ppm) are included for comparison. Phosphoric acid stabiliser was added to give 16 or 32 ppm based on weight of prepolymer.

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Results for polymer made using the catalysts prepared according to Examples 3 to 8, based on a total metal addition level of 30 ppm, are given in Table 2 below in which results on polymer using germanium oxalate [Geoxal] at a level of 100 ppm Ge and  $\text{Sb}(\text{OAc})_3$  at Sb level of 250 ppm are given for comparison. Phosphoric acid stabiliser was added to give 32 ppm based on weight of prepolymer.

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#### Example 12

The catalysts were used to prepare polyethylene terephthalate (PET) in a larger reactor. Ethylene glycol (2.04 kg) and terephthalic acid (4.55 kg) were charged to a stirred, jacketed reactor. The catalyst and other additives were added and the reactor heated to  $226 - 252^\circ\text{C}$  at a pressure of 40 psi to initiate the first stage direct esterification (DE) process. Water was removed as it was formed with recirculation of the ethylene glycol. On completion of the DE reaction the contents of the reactor were allowed to reach atmospheric pressure before a vacuum was steadily applied. The stabilisers were

added and the mixture heated to  $290 \pm 2^\circ\text{C}$  under vacuum to remove ethylene glycol and yield polyethylene terephthalate. The final polyester was discharged once a constant torque had been reached which indicated an IV of around 0.62. The properties of the polymers were measured as described in Example 11 and are reported in Table 3.

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The glass transition temperatures  $T_g$  show similar values. The onset of crystallisation (heating)  $T_{no}$  and  $T_n$  crystallisation peak (heating) show similar values, Example 4 however shows slightly lower values.

Example 3 and Example 4 show standard recrystallisation enthalpies on cooling. The germanium solution and Examples 5 and 6 show reduced crystallinity levels and relatively low recrystallisation temps ( $T_c$  and  $T_{co}$ ). This reduction in overall crystallinity indicates clean polymers. With this in mind Examples 5 and 6 mixed Ge/Ti systems have better (lower)  $T_{co}$ ,  $T_c$  values than 100% Ge citrate catalyst.

15 The titanium - germanium mixed catalyst compositions of the invention have the advantage of requiring considerably less germanium metal than is usually used for making polyesters which has considerable economic benefit because germanium is a very expensive metal in comparison with titanium or antimony. The Examples demonstrate that titanium - germanium catalysts usually produce polyester with improved colour compared with the polyester produced using the titanium only catalyst with similar ligand chemistry prepared in Example 9. These catalysts also unexpectedly usually produce polyester at faster rates than polyester produced using the titanium only catalysts with similar ligand chemistry in Example 9.

The titanium - antimony catalysts have the advantage of requiring considerably less antimony metal. 25 The high levels of antimony required in conventional polyester reactions using antimony only catalysts (typically 250 to 350 ppm) leave considerable residues in the polyester which can cause blockages in downstream processing equipment such as spinnerets, cause unsightly haze in bottles and also cause crystallisation problems in the finished polymer. The titanium - antimony catalysts shown in Example 10 produces polyester with improved colour compared with the polyester produced using titanium only catalysts with similar ligand chemistry in Example 9. The titanium - antimony catalysts shown 30 Example 10 also unexpectedly produces polyester at a faster rate than polyester produced using titanium only catalyst in Example 9.

Table 1

Catalyst	P (ppm)	Ti (ppm)	Ge (ppm)	Reaction time (min)	I.V.	L*	a*	b*	OH ends	DEG wt%	VEG	Mw	Mn	Tp	Tg	Tn	Tc
*Sb(OAc) <sub>3</sub>	32	-	-	160	0.56	64.82	-0.93	17.80	1.26	2.85	0.0113	41300	22400	245	72	140	169
Example 1	32	30	5	155	0.44	61.16	1.51	23.54	1.92	2.55	0.0144	41700	17200	248	70	130	199
Example 1	16	30	5	145	0.55	47.12	6.86	26.81	1.54	2.72	0.0127	43000	18400	245	73	135	193
Example 2	32	30	404	150	0.56	51.58	7.23	28.90	1.05	2.70	0.0183	72100	36800	246	72	128	200
Example 2	16	30	404	150	0.59	48.46	7.19	27.91	0.90	2.83	0.0295	70700	28900	244	73	132	195

Table 2

Catalyst	P (ppm)	Ti (ppm)	Ge (ppm)	Reaction time (min)	I.V.	L*	a*	b*	OH ends	DEG wt%	VEG	Mw	Mn	Tp	Tg	Tn	Tc
*Ge-citrate	32	-	100	210	0.53	68.30	-1.2	14.2									
*Sb(OAc) <sub>3</sub>	32	-	-	160	0.56	64.82	-0.93	17.80	1.26	2.85	0.0113	41300	22400	245	72	140	169
Example 3	32	25.7	4.3	210	0.53	62.81	-0.35	20.03	1.15	2.55	0.138	73200	33600	247	71	137	179
Example 4	32	20.0	10.0	210	0.36	64.50	-0.46	14.51	2.55	2.53	0.0267	39100	19700	248	70	130	200
Example 5	32	12.0	18.0	210	0.50	66.62	-2.18	14.00	1.15	2.61	0.101	69400	33100	246	72	139	161
Example 6	32	5.4	24.6	210	0.44	68.25	-1.52	14.26	1.91	2.78	0.0397	54000	29500	247	72	140	173
Example 7	32	19.9	10.1	150	0.45	53.25	5.05	28.47	1.40	2.70	0.0485	58300	29400	247	69	133	186
Example 8	32	5.4	24.6	180	0.49	65.66	-1.32	14.49	2.95	2.65	0.0632	41600	14200	246	68	134	190

Table 3

Catalyst	P (ppm)	Ti (ppm)	Ge (ppm)	DE Time (mins)	PC Time (mins)	5 mins				20 mins				Tp	Tg	Tno	Tc
						L*	a*	b*	L*	a*	b*	L*	a*				
Example 3	10	26	4.3	94	100	67.1	-2.5	21.4	67.3	-1.3	24.8	67.3	-1.3	246	75	144	181
Example 6	5	7.5	34	86	123	70.7	-3.4	13.2	67.5	0.2	21.5	67.5	0.2	246	74	143	162
Example 4	10	15	7.5	90	154	64.9	-2.3	23.6	63.6	0.6	25.2	63.6	0.6	246	75	139	184
Example 5	5	7.5	11.3	76	120	71.5	-3.1	12.2	64.6	-0.3	20.6	64.6	-0.3	247	75	143	163
*Germanium citrate	10	-	150	85	141	69.3	-1.0	9.2	70.4	-1.3	12.2	70.4	-1.3	N/A	N/A	N/A	N/A
*Example 10	10	15	0	95	130	71.6	-2.6	17.7	73.6	-2.1	25.9	73.6	-2.1	N/A	N/A	N/A	N/A
Example 11	10	15	7.6 Sb	99	104	64.6	-1.5	10.0	58.6	-1.3	11.2	58.6	-1.3	N/A	N/A	N/A	N/A
*Sb tris-glycolate	10	0	300 Sb	100	130				65.6	-2.3	6.3	65.6	-2.3	N/A	N/A	N/A	N/A

\* denotes comparative examples.

Tg = polymer glass transition temperature, T<sub>no</sub> = onset of crystallisation (heating), Tp = melting point, Tc = crystallisation (cooling).

Claims

1. A catalyst composition suitable for use as a catalyst for the preparation of an ester comprising an organometallic compound which is a complex of
  - (a) a first metal selected from the group consisting of titanium and zirconium,
  - (b) a second metal selected from the group consisting of germanium, antimony and tin and
  - (c) a carboxylic acid.
2. A catalyst composition as claimed in claim 1, wherein the molar ratio of first metal to second metal is in the range 99 : 1 to 1 : 99.
3. A catalyst composition as claimed in claim 1 or claim 2, wherein said carboxylic acid comprises an unsubstituted  $C_1 - C_{20}$  carboxylic acid or a hydroxy carboxylic acid having one or more carboxylic acid groups.
4. A catalyst composition as claimed in claim 3, wherein said carboxylic acid is selected from the group consisting of acetic acid, oxalic acid, capric acid, lauric acid, lactic acid, citric acid, malic acid and tartaric acid.
5. A catalyst composition as claimed in any preceding claim, wherein the molar ratio of acid to total metal in the complex is from 4 : 1 to 0.1 : 1.
6. A catalyst composition as claimed in any preceding claim, further comprising a solubilising compound.
7. A catalyst composition as claimed in any preceding claim, wherein said solubilising compound is an alcohol containing at least two hydroxyl groups.
8. A catalyst composition as claimed in claim 7, wherein said alcohol is a dihydric alcohol which is selected from 1,2-ethanediol, 1,2-propanediol, 1,3-propanediol, 1,4-butanediol, 2-methyl-2,4-pentanediol, cyclohexane dimethanol, diethylene glycol or a polyethylene glycol.
9. A catalyst composition as claimed in claim 7 or claim 8, wherein said alcohol is present in the complex in a ratio of from 50 to 1 moles of alcohol to each mole of total metal.
10. A catalyst composition as claimed in any preceding claim, further comprising a base.



11. A catalyst composition as claimed in claim 10, wherein said base is selected from sodium hydroxide, potassium hydroxide, calcium hydroxide, ammonium hydroxide, tetrabutyl ammonium hydroxide, tetraethyl ammonium hydroxide (TEAH), choline hydroxide (trimethyl(2-hydroxyethyl)ammonium hydroxide), benzyltrimethyl ammonium hydroxide, monoethanolamine, diethanolamine, triethanolamine or triisopropanolamine..
12. A catalyst composition as claimed in claim 10 or claim 11, wherein, the amount of base used is in the range 10 to 0.1 moles of base per mole of total metal.
13. A catalyst composition as claimed in any preceding claim, wherein the source of the first metal is an orthoester or condensed orthoester of titanium or zirconium.
14. A catalyst composition as claimed in any preceding claim, wherein the source of the second metal is an oxide, halide or metal-organic compound of germanium, antimony or tin.
15. A catalyst composition as claimed in any preceding claim, wherein the catalyst composition is derived from an alkoxide of the second metal.
16. A method of preparing a catalyst composition comprising the steps of :-
  - a) adding to an aqueous carboxylic acid solution an alkoxide of a first metal selected from titanium and zirconium and, separately, a compound of a second metal selected from germanium, antimony or tin;
  - b) removing from said mixture water and free alcohol formed in the reaction between said metal alkoxides and the carboxylic acid;
  - c) optionally adding to the resulting composition a base and/or an alcohol containing at least two hydroxyl groups;
  - d) optionally removing from the composition excess water added with the components in step (c).
17. A method of preparing a catalyst composition as claimed in claim 16, wherein said compound of a second metal comprises an alkoxide, oxide, halide or organic salt.
18. A method of preparing a catalyst composition comprising the steps of :-
  - a) preparing a solution of a carboxylic acid salt of a second metal selected from germanium, antimony and tin, optionally in the presence of an alcohol containing at least two hydroxyl groups;
  - b) reacting together an orthoester of a first metal selected from titanium and zirconium, optionally, a base and/or an alcohol containing at least two hydroxyl groups;

- c) adding the reaction product formed in (b) above to the solution prepared in (a) above, with mixing,
  - d) optionally removing from the composition excess water and/or alcohol formed in step (c).
19. A process for the preparation of an ester comprising the step of carrying out an esterification reaction in the presence of a catalyst composition comprising an organometallic compound which is a complex of a first metal selected from the group consisting of titanium and zirconium, a second metal selected from the group consisting of germanium, antimony and tin, and a carboxylic acid.
20. A process as claimed in claim 19, wherein said esterification reaction comprises:-
- (i) a direct esterification in which a carboxylic acid or its anhydride and an alcohol react to form an ester or
  - (ii) a transesterification (alcoholysis) in which a first alcohol reacts with a first ester to produce an ester of the first alcohol and a second alcohol produced by cleavage of the first ester or
  - (iii) a transesterification reaction in which two esters are reacted to form two different esters by exchange of alkoxy radicals or
  - (iv) a polyesterification comprising the reaction of at least one polybasic acid with at least one polyhydric alcohol.
21. A process for the manufacture of a polyester comprising the steps of:
- (i) reacting together a compound selected from the group consisting of terephthalic acid, dimethyl terephthalate, isophthalic acid, dimethyl isophthalate, dimethyl 2,6 naphthalate or naphthalene dicarboxylic acid with an alcohol selected from the group consisting of 1,2-ethanediol, 1,4-butanediol, 2,3-propanediol, 1,6-hexanediol, trimethylol-propane and pentaerythritol in the presence of a catalyst composition comprising an organometallic compound which is a complex of a first metal selected from the group consisting of titanium and zirconium, a second metal selected from the group consisting of germanium, antimony and tin, and a carboxylic acid
  - (ii) optionally subjecting the resulting polymer to a solid phase polymerisation reaction, to form a polyester material having an intrinsic viscosity of at least 0.5 dl/g, as measured by the method of ASTM D-4603.
22. A polyester article containing residues of a catalyst composition comprising an organometallic compound which is a complex of
- (a) a first metal selected from the group consisting of titanium and zirconium,
  - (b) a second metal selected from the group consisting of germanium, antimony and tin and
  - (c) a carboxylic acid.

23 A polyester article as claimed in claim 21, which is a fibre, film or container.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 01/00001

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J31/04 B01J31/12 C08G63/82 C08G63/84 C08G63/85

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☐ Further documents are listed in the continuation of box C.

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